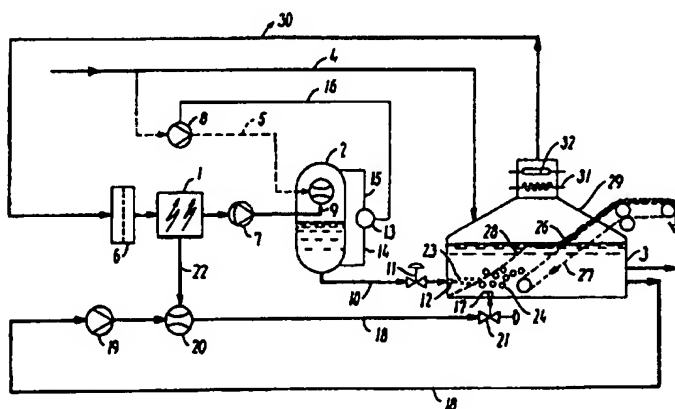




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C02F 1/78, 1/24	A1	(11) International Publication Number: WO 97/29997 (43) International Publication Date: 21 August 1997 (21.08.97)
(21) International Application Number: PCT/DK97/00061 (22) International Filing Date: 11 February 1997 (11.02.97) (30) Priority Data: 0145/96 12 February 1996 (12.02.96) DK (71) Applicant (for all designated States except US): AQUA SYSTEM A/S [DK/DK]; Avnvej 14, DK-7400 Herning (DK). (72) Inventor; and (75) Inventor/Applicant (for US only): KAAS, Povl [DK/DK]; T.H. Nielsens Gade 11G, DK-7400 Herning (DK). (74) Agent: HOLME, Edvard; Holme Patent a/s, Sankt Pederstræde 41, DK-1453 København K (DK).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> <i>In English translation (filed in Danish).</i>

(54) Title: METHOD AND PLANT FOR PURIFICATION OF CONTAMINATED WATER

**(57) Abstract**

A method and a plant serving the purpose of purifying water with ozone from especially oxidizable impurities. The plant comprises a purification basin (3) for the contaminated water, an ozone source (1) for, when in operation, supplying the plant with ozone for purification of the water, a reaction container (2), which, when in operation, partly is supplied with water from a water source to a predetermined level in the container by means of a first pressure pump (8), partly is supplied with ozone under pressure from the ozone source via a gas conduit with a second pressure pump (7), which preferably is a spark-free membrane pump. At the bottom of the basin is placed a first set of nozzles (12) which via at least one first water conduit (10) is connected to the water in the reaction container. A second set of nozzles (17) which, at the bottom are placed in the basin at a distance from the first set of nozzles, are connected to at least one second water conduit (18) which is connected to the ozone source as well as to a water source and has a third pressure pump (19) for, when in operation, driving the water through the conduit with a pressure which is smaller than the pressure in the reaction container. The plant can with less use of ozone efficiently purify the water from impurities. The additional ozone is recycled in an economic expedient way instead of being released into the environment and endangering the surroundings. Suspended and dissolved impurities in the waste water can be brought to flocculate without addition of chemicals.

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Method and plant for purification of contaminated water.

5 The invention concerns a method for purification of contaminated water from especially oxidizable impurities.

Contaminated water is led out in great amounts as sewage from, for example, households and industries. It is required that the impurities of the sewage is removed to an excessively extend, before the water is released to the recipient. This purification takes place, for example, in the municipal plant, where a number of processes is being used to remove and neutralize the impurities of the sewage. A common part of the purification process is that the impurities are brought to flocculate in great basins with chemicals, which are added to the water. The created flocs are precipitated as sludge, which is removed by means of, e.g. scrapers.

15 The impurities can consist of organic substances, pesticides, tensides, organic and chemical solvents and colour residues. It is known that water, which is contaminated with such substances, can be purified by means of ozone, which usually in the form of bubbles rising through the water, exposes the substances to heavy oxidation. Thereby the substances are precipitated as particles which can be removed by means of a filter or similar device.

20 The conventional ozone purification plants thus known have, however, a disproportionately large expenditure of ozone in relation to the purification effect obtained, and the reaction time is very long causing the necessity to use very large and expensive reaction basins. Further, the additional ozone is led out to the environment endangering person, who might be in the surroundings.

25 The object of the invention is to provide a method of the prior cited type, which with less use of ozone and more efficient than previously known, can purify the contaminated water.

30 A second object of the invention is to provide a method of the prior cited type, being adapted in such a way that the additional ozone is not released to the surroundings.

A third object of the invention is to provide a method of the prior cited type, by means of which suspended and dissolved impurities in the sewage are brought to flocculate without addition of chemicals.

35 The new and unique by means of which this is obtained according to the invention, is that the contaminated water is led into a purification basin, where there at a first set lead-

A third object of the invention is to provide a method of the prior cited type, by means of which suspended and dissolved impurities in the sewage are brought to flocculate without addition of chemicals.

5 The new and unique by means of which this is obtained according to the invention, is that the contaminated water is led into a purification basin, where there at a first set lead-in's, which in reciprocal distance are dispersed between two of the opposite sides of the basin and preferably are situated near the bottom of the basin, ozone is supplied in the form of small, fine bubbles, and that there at a second set of lead-in's at distance from the first set of lead-in's, and equally preferably near the bottom of the basin, ozone is supplied in the form of bubbles, which are substantially larger than the first mentioned fine bubbles.

10 The small, fine bubbles have in combination a exceedingly large tangent surface with the water and the ozone is therefore quickly and efficiently brought to process large amounts of impurities. The reaction products are almost momentarily forming a shell around each of the fine bubbles, which at the same time loose buoyancy, due to the reduced contents of ozone in the bubbles as the ozone, to a larger or smaller degree, is used for the reaction.

15 The fine bubbles with their shell of reaction products will therefore not change level substantially, while they are pushed across the bottom of the basin by new fine bubbles, which in a continuous stream are led into the basin. During this process the fine bubbles are colliding with the rising large bubbles, whereby each one of the large bubbles is catching an amount of fine bubbles. The bubbles merge, and the shell around the many fine bubbles are now settling as a whole shell around the large bubbles. During the continuous rising through the water, the ozone content of the large bubbles will to a greater or smaller extend be used for a continuous reaction with the substances not finished to react in the surrounding shell, and for the reaction with fresh impurities in the water. When the bubbles have reached the surface, they will break, whereby the remaining ozone is set free, while the shells are collapsing and form flocs which easily can be removed by means of, e.g. a belt filter for micro filtration. As it can be seen, these flocs are thus created without use of those chemicals which normally are used to flocculation in the conventional plants.

20 The finest bubbles, and thereby the most efficient purification of the contaminated water, are obtained, when they are created through an overpressure to drive water, which is supersaturated with ozone, into the contaminated water through 35 nozzles which are placed in the basin.

The invention also concerns a plant for purification of contaminated water for especially oxidizable impurities, and which comprises a purification basin for the contaminated water, an ozone source for, when in operation, providing the plant with ozone for purifying the water, a reaction container, which, when in operation, partly is supplied with water from a water source to a predetermined level in the container by means of a first pressure pump, partly is supplied with ozone under pressure from the ozone source via a gas conduit by means of a second pressure pump, which preferable is a sparkfree membrane pump, a first set of nozzles, which preferably at the bottom are place in the basin between two of the opposite sides of this basin, and which via at least a first water conduit are connected to the water in the reaction container, a second set of nozzles, which preferably at the bottom are placed in the basin at a distance from the first set of nozzles, and which are connected to at least one other water conduit, which is connected to as well the ozone source as to a water source and having a third pressure pump to drive the water, when in operation, through the pipe with a pressure which preferably is smaller than the pressure in the reaction container. This plant is suitable to perform the procedure according to the invention.

The water which is added to the reaction container, can with advantage be the contaminated water. In some cases the whole water stream can be brought to pass the reaction container, where then an initial purification process will take place, and at the same time the water will be enriched with ozone. When greater water volumes are to be purified, it will, however, for practical reasons be much more expedient to let only part of the contaminated water run through the reaction container.

In order to obtain optimum effect, the water in the reaction container will have to absorb as much ozone as possible, and the pressure in the container must be relatively high, e.g. 10 bar. At such high pressures there is a risk that the ozone will explode, and as pressure pump for pumping the ozone from the ozone source to the reaction container, a membrane pump of sparkfree plastic can therefore expediently be used.

The injection into a container will normally be connected with a danger of explosion, but this danger can be eliminated by having the water stream into the reaction container via an ejector which fills the space above the water surface with a fog of water and steam. An explosion cannot occur in such a wet atmosphere.

By an expedient embodiment the ozone is led into the reaction container via the suction side zone, whereby it can be ensured at its optimum that the inflow of the ozone into the reaction container takes place in a wet atmosphere. A second advantage which is obtained by means of this method, consists of the

fact that the ozone quickly is suspended in the form of fine bubbles in the water and/or is dissolved in the water.

By inserting an ejector in the second water conduit, which is connected to the second set of nozzles, and connecting the ozone source to the suction side of this ejector, the same advantages can be obtained as described above regarding the explosion security and quick and efficient suspension and/or dissolution of the ozone in the water, which is driven into the basin via the second set of nozzles.

When the water in the reaction container is supersaturated with ozone under high pressure and by that means is filled with enormous amounts of small fine bubbles, there is no longer buoyancy in the water. A float will sink to the bottom. The level of the water surface can, consequently, not as usual be registered by means of a float.

Such a registration is, however, of great importance to the secure and efficient function of the plant. Thus, the ejector will be stifled if the water rises so much that it will be flooded. If the reaction container, on the other hand, is emptied for water, the ozone will stream directly into the basin. The plant cannot operate securely and efficiently under these circumstances.

According to the invention the level of the water surface is indirectly registered by means of a pressure difference gauge, which continuously measures the difference in pressure between the top and the bottom of the reaction container. The measured difference in pressure is a measure for the height of the water column. The pressure difference gauge is then adjusted, by deviations from a given set value, which represents the predetermined height of the water column, to give a signal to the first pressure pump to pump more or less water into the reaction container in dependence of the present value of the signal.

The sewage volume can vary with the time, and the same applies to the degree of contamination. The purification process cannot go at its optimum, if there during the changing conditions all the time is sent the same amount of ozon enriched water through a set of nozzles. According to the invention there is therefore in the water conduits for each of the two sets of nozzles inserted a valve for regulating the pressure and/or volume of the water which is added.

As earlier mentioned, an leak of ozone can endanger the persons in the surroundings of the plant. According to the invention the purification basin is covered with a bellshaped cover for collection of additional ozone from the purification process. The collected ozone is, mixed with the existing air in the bassin, led past a cooler for drying of the air mixture, which then is sent past at least one UV lamp, whereby the

ozone is converted into oxygen. The air mixture, which now has a large contents of oxygen, is now streaming through a gas conduit to an oxygen membrane, which only allows oxygen molecules to pass. The oxygen deriving from this process, is finally used in an ozone generator for the production of new ozone for the process. With this arrangement the necessity of having to leak additional ozone to the surroundings will be eliminated. At the same time the process is cost saving, since the additional ozone expediently can be used again in a closed cycle.

The invention will be explained more fully by the following description of embodiment, which just serves as example, with reference to the drawing, where

Fig. 1 diagrammatically shows a plant according to the invention to purify contaminated water, and

Fig. 2 schematically shows in principle an embodiment of the purification process according to the invention.

The main components in the purification plant shown in fig. 1 is a ozone generator 1, a reaction container 2 and a purification basin 3. The contaminated water, which is to be purified, is in the case shown led into a main stream 4 to the purification basin 3 and in a secondary stream 5, which is drawn with a dotted line, to the reaction container 2.

The contaminated water can derive from many different sources. For example, the fish industry or other foodstuffs factories with sewage, which typically has a large contents of organic substances. The purification process can advantageously be a part of a larger process, where, in one or more previous steps solidstate substances as e.g. gravel and sand is removed, and in the succeeding steps for example nitrite will be removed.

The plant operates with ozone as the sole purification mean. The ozone is produced in the ozone generator 1 by oxygen coming from an oxygen membrane 6, which only allows the contents of oxygen molecules of the air to pass. The ozone generator can, for example, be of the type, which uses a high voltage area to influence a current of dry oxygen or air with electrical discharges, whereby a part of the oxygen molecules are decomposed to free atoms.

Oxygen atoms connecting with present oxygen molecules forms the ozone. The formed ozone is pumped by a membrane pump 7, consisting of a sparksafe type of plastic, into the reaction container under a high pressure, e.g. 10 bar.

The secondary stream 5 of contaminated water is pumped by a pressure pump 8 into the reaction container 2 via an ejector 9 under equally high pressure. The ejector will in this process

suck in ozone, which thereby quickly and efficiently will be suspended in the form of fine bubbles in the water and/or be dissolved in the water. The ozone enriched water will via a water conduit 10 with a regulation valve 11 be led into the purification basin 3 via a first set of nozzles 12.

- 5 According to the invention the amount of ozone pumped into the reaction container must be at a level, in relation to the water volume pumped in at the same time, that the water is supersaturated with ozone under a high pressure. The water in the reaction container is therefore filled with an enormous amount of very small, fine bubbles, which in the following will be referred to as microbubbles. Due to the presence of the microbubbles a float will sink to the bottom in the water.
- 10 It is, however, with reasonable limits, necessary to be able to fix the height of the water surface in the reaction container. If the water surface is rising above a certain height, the ejector will be flooded, and not able to function as presupposed. If the container is emptied, there will via the water conduit 10, the regulation valve 11 and the nozzles 12 stream ozone directly into the purification basin 3, so that
- 15 the aimed purification process is prohibited.

- The plant according to the invention comprises therefore a pressure difference gauge 13, which via cables 14 and 15 measures the pressure in the top and at the bottom, respectively, of the reaction container, and registers the difference in pressure. The difference in pressure represents the height of the water column, and the pressure difference gauge is therefore
- 20 adjusted with a set value, which is equal to a predetermined height. If the registered difference pressure at a given moment deviates from this set value, the pressure difference gauge will via a cable 16 send a signal to the pressure pump 8 to increase or decrease the water volume, until the registered deviation from the set value is zero, and the water surface therefore will be at the predetermined level in the reaction
- 25 container 2.

- The first set of nozzles 12 are, as shown, placed in the wall of the purification basin and near the bottom. At some distance from this set of nozzles there is likewise at the bottom placed a second set of nozzles 17, which are supplied with ozone enriched water via a water conduit 18, in which there is
- 30 inserted a pressure pump 19, an ejector 20 and a regulation valve 21.

- The ozone generator 1 is via a cable 22 connected to the suction side of the ejector 20, whereby the water in the cable 18 is enriched with ozone. As shown, the water is streaming in the water conduit 18 in this case in a circuit from the purification basin with purified water and back again to the purification basin with ozone enriched water. In other cases the
- 35 water supplied by the second set of nozzles can, however, come from a different source.

The special mode of operation is explained in fig. 2, which in principle shows the process in the purification basin 3.

Ozone enriched water is pressed under high pressure, e.g. 10 bar, via the water conduit 10 and the first set of nozzles 12 into the contaminated water in the purification basin 3 near the bottom 25 of the basin. Further, ozone enriched water is pressed under somewhat lower pressure, e.g. 3 bar, via the water conduit 18 and the second set of nozzles 17 at the bottom 25 in a distance from the first set of nozzles 12, into the contaminated water in the purification basin 3. Pressure, ozonebearing and nozzle construction are adjusted in such a way that there at the first set of nozzles arise fine bubbles or microbubbles 23 and at the second set of nozzles large bubbles or macrobubbles 24.

The microbubbles, which are in an enormous amount and to a substantial degree already have been formed in the reaction container 2, have, if combined, an enormous surface, and their aggressive ozone content begin immediately to react with the surrounding impurities in the water. Fig. 2 is very simplified and shows only one single microbubble in its various development stages, during which there succeedingly is formed a shell of reaction products around the bubble. At the same time the ozone content is completely or partly used in the process and will therefore not, as could be expected, rise in the water, but are instead being displaced to the right (in the figure) by the succeeding microbubbles, which continuously stream in through the nozzles 12.

The macrobubbles 24 from the nozzles 17 run equally through a number of development stages, while they as shown rise from the bottom to the water surface. In this process they encounter a lot of microbubbles and merge. The shells of the microbubbles will form a new shell around the ascending macrobubbles, and the remaining ozone content will at the same time process non-processed substances in the shell and not yet processed impurities in the water.

The content of ozone in the macrobubbles will therefore gradually be reduced, as the shell increases. At the surface the bubbles will burst and the shells will collapse to flocs 26, while the remaining ozone in the bubbles is released.

As shown in fig. 1 the flocs 26 are removed by means of a belt filter for microfiltration 27 of the type described in the applicants' Danish Patent Application No. 0145/96, to which is referred as a reference.

The microbubbles 23 are so fine, that they are not visible to the naked eye but are manifested as a milky white fog in the water. To the left of the dotted line of the purification basin 3 in fig. 1 the water is milky white and therefore filled

with microbubbles. To the right of the line 28 the milky fog has disappeared, which signify that the contents of ozone in the bubbles is used in the reactions processes and/or that the microbubbles have merged.

5 The purification process will normally not use the supplied amount of ozone to the fullest extend. The additional ozone will therefore accumulate under a bellshaped cover 29, covering the purification basin 23. The accumulated ozone is, mixed with air, led from the bellshaped cover and by a cooler 30, which cools off and consequently dries the air mixture. The dried air mixture is then led past a number of UV lamps, which by radiation decomposes the ozone to oxygen. The dry, oxygen enriched air mixture is finally led, via a gas conduit 10 30, to the oxygen membrane 6, which detains all other gasses but oxygen, which, as previously described, is used as raw material in the ozone generator 1 for the production of ozone for the purification process.

15 The additional ozone is thus being recycled in the plant and is reused repeatedly economic expedient instead of being released into the invironment where the ozone could be harmful to persons in the surroundings.

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Claims:

1. Method for purification of contaminated water from especially oxidizable impurities using ozone, characterized in,
 - 5 - that the contaminated water is placed in a purification basin,
 - that the contaminated water, at a first set of lead-in's, which in reciprocal distance are dispersed between two of the opposite sides of the basin and preferable near the bottom of the basin, is supplied with ozone in the form of
10 small, fine bubbles,
 - that the contaminated water at the second set of lead-in's at distance from the first set of lead-in's, and equally preferably near the bottom of the basin is supplied with ozone in the form of bubbles, which are substantially larger than the first mentioned fine bubbles.
15
2. Method according to claim 1, characterized in, that at least the small ozone bubbles are added to the contaminated water in the waterbasin, which is supersaturated with ozone, and which is driven through nozzles being placed at the respective lead-in's.
3. Plant for, ozone-purification of contaminated water for
20 especially oxidizable impurities, characterized in that it comprises
 - a purification basin for the contaminated water,
 - 25 - an ozone source for, when in operation, supplying ozone to the plant for purification of the water,
 - a reaction container, which, when in operation, partly is supplied with water from a water source up to a predetermined level in the container by means of a first pressure pump, partly is supplied with ozone under pressure from the
30 ozone source via a gas conduit with a second pressure pump, which preferably is a sparkfree membrane pump,
 - a first set of nozzles, which preferably are placed in the basin between the two opposite side of this latter, and which via at least one first water conduit is connected to
35 the water in the reaction container,

- a second set of nozzles, which preferably at the bottom are placed in the basin at distance from the first set of nozzles, being connected to at least one second water conduit, which is connected as well to the ozone source as to a water source and having a third pressure pump for, when in operation, driving the water through the conduit with a pressure, which preferably is smaller than the pressure in the reaction container.
- 5
4. A plant according to claim 1, characterized in that the water source, when in operation for supplying the reaction container with water, is the contaminated water or a part of this.
- 10
5. A plant according to claim 3 or 4, characterized in that the water is supplied to the reaction container via at least one ejector or similar device, which has been placed at a distance above the surface of the water.
6. A plant according to claim 3, 4 or 5, characterized in that there in the second water conduit, which is connected to the second set of nozzles, is inserted at least one ejector or similar device, which at the sucking side is connected to the ozone source.
- 15
7. A plant according to each of the claims 3 - 6, characterized in that it comprises a pressure difference gauge for measuring the pressure difference between the top and the bottom of the reaction container and for, in dependence of the measured pressure difference, signal for regulation of the first pressure pump, which serves, when in operation, the purpose of pumping water from a water source to the reaction container.
- 20
8. A plant according to each of the claims 3 - 7, characterized in that there in the first and/or the second water conduit for supply of water to the first and the second set of nozzles, respectively, in the purification basin, or in both of these water conduits, a valve for regulation of the pressure and/or volume of the supplied water has been inserted.
- 25
9. A plant according to each of the claims 3 - 8, characterized in that the purification basin is covered with a bellformed cover for collecting the additional ozone from the purification process, and that the top of the bell is connected to the ozone source via a cooler for drying of the passing gasses, at least one UV lamp for decomposing ozone to oxygen and a gas conduit with an inserted oxygen membrane.
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10. A plant according to each of the claims 3 - 9, characterized in that a belt filter for microfiltration has
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been placed in the purification basin, when in operation, to remove solids from the water.

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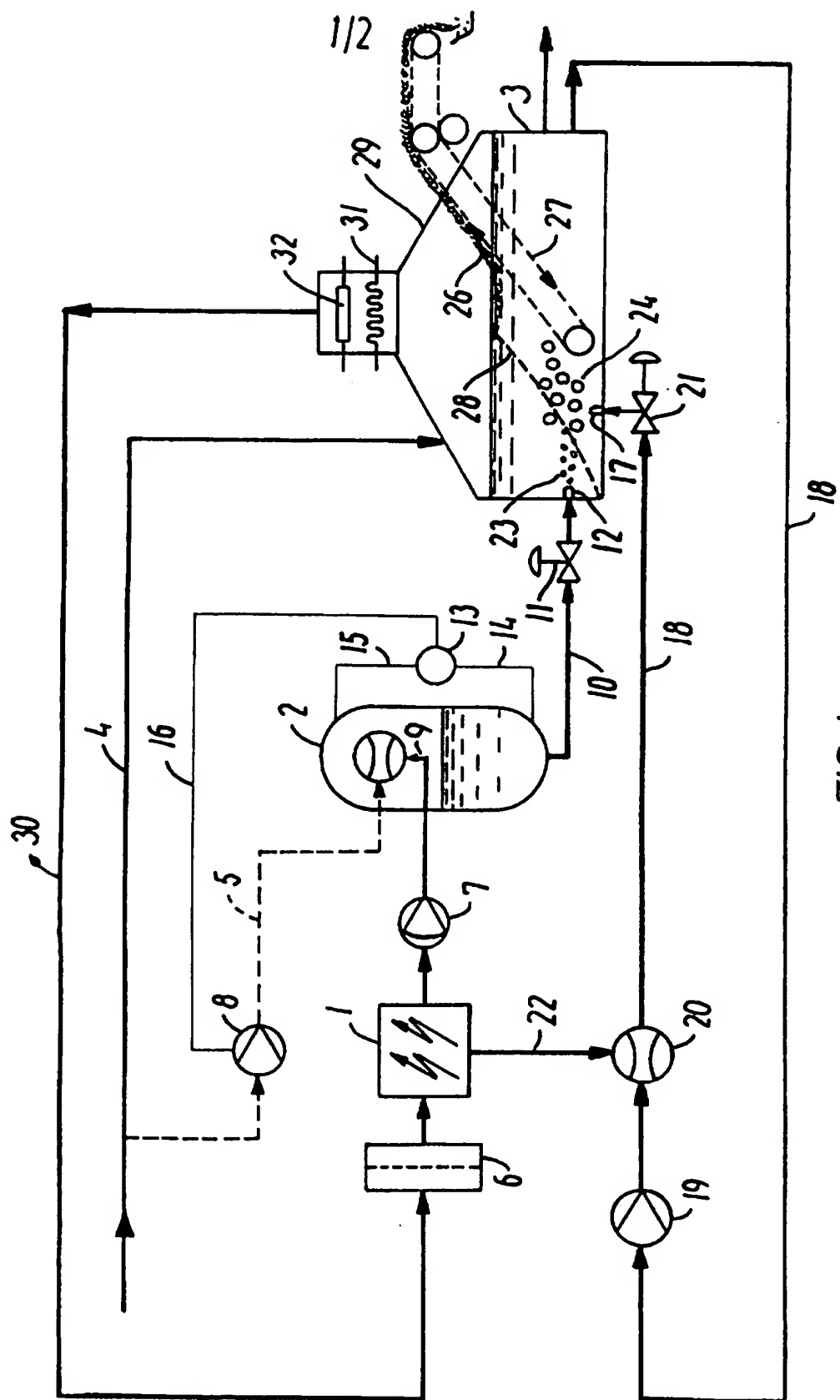
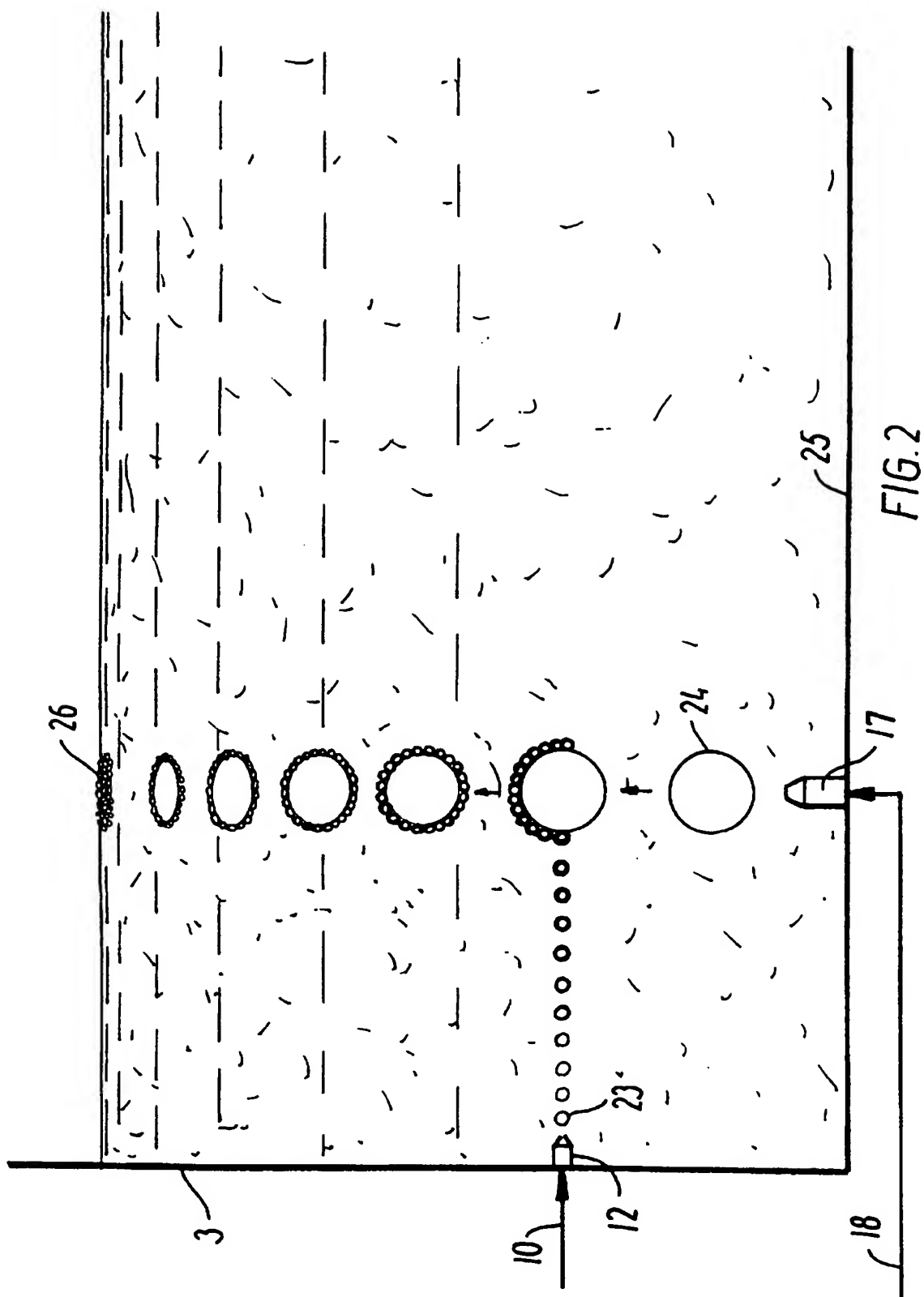


FIG. 1

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 97/00061

A. CLASSIFICATION OF SUBJECT MATTER		
IPC6: C02F 1/78, C02F 1/24 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC6: C02F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
SE,DK,FI,NO classes as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0570756 A1 (MESSER GRIESHEIM GMBH), 24 November 1993 (24.11.93), column 2, line 36 - line 40, claim 1 --	9
A	EP 0250316 A1 (OTV OMNIUM DE TRAITEMENTS ET DE VALORISATION), 23 December 1987 (23.12.87), figure 1, claim 1 --	1
A	Patent Abstracts of Japan, Vol 12, No 446, C-546, abstract of JP,A,63-171694 (KATSUMI TAKAO), 15 July 1988 (15.07.88) --	3
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
23 June 1997		27.06.1997
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 97/00061

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CH 507874 A (WESTINGHOUSE ELECTRIC CORPORATION), 15 July 1971 (15.07.71), claim 1 --	1
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Information on patent family members

03/06/97

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